

UNITED STATES PATENT OFFICE

1,993,513

TREATMENT OF HYDROCARBONS

Vladimir Ipatieff, Chicago, Ill., assignor to Universal Oil Products Company, Chicago, Ill., a corporation of Delaware

No Drawing. Application July 3, 1933,
Serial No. 678,933

9 Claims. (Cl. 196—10)

This invention relates more particularly to the treatment of olefinic hydrocarbons which are normally gaseous at ordinary temperatures and pressures.

general character of the compounds treated by the present process. It is not complete but is introduced as a matter of reference.

Olefinic hydrocarbons with which the present invention is concerned occur along with corresponding paraffinic or saturated hydrocarbons in commercial hydrocarbon mixtures such as those encountered in the cracking of petroleum, in gas making processes and as by-products in various chemical industries. In general they are more chemically active than other classes of hydrocarbons, particularly if they contain more than one double bond or triple bonds between carbon atoms. Even when under mild catalytic influence they exhibit this reactivity in their pronounced tendency to polymerize and form substances of higher molecular weight.

Olefins occur in particularly large percentages in the fixed gases from cracking processes as well as in the gasoline boiling range fractions. The fixed gases are utilized principally as fuel, only a very small percentage of present day commercial production being subjected to processes for the recovery or utilization of the olefinic constituents. The manufacture of secondary alcohols such as iso-propyl alcohol and others by first absorbing the corresponding olefins in cracked gases in sulfuric acid and then hydrolyzing the acid esters has been undertaken to a limited extent. The olefins present in cracked hydrocarbon mixtures of gasoline boiling range are of moderately high anti-knock value, but a certain percentage of these is too highly unsaturated, and these must be removed by chemical treatment, usually with sulfuric acid, to insure proper stability of the gasoline under storage conditions.

The present process provides for more effectively utilizing the olefinic constituents of commercial hydrocarbon mixtures, particularly those occurring in the gases from oil cracking processes to produce valuable derivatives therefrom and it may also be applied to individual olefins produced by special chemical methods or by fractionation of mixtures.

In one specific embodiment the invention comprises treatment of normally gaseous olefin hydrocarbons at elevated temperatures to produce polymers therefrom utilizable as constituents of motor fuel with solid contact materials or catalysts comprising phosphoric acid and siliceous carrying or spacing materials of a porous and adsorptive character.

The following table is introduced to show the

Compounds	Formula	Boiling point °C.
Ethylene.....	$\text{CH}_2=\text{CH}_2$	-105
Propylene.....	$\text{CH}_3\text{CH}=\text{CH}_2$	-48
Ethyl ethylene.....	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}_2$	-5
Plane-sym. dimethyl ethyl- Axial-sym. ethylene.....	$\text{CH}_3\text{CH}=\text{CH}\cdot\text{CH}_3$	+1
Unsym. dimethyl ethylene.....	$(\text{CH}_3)_2\text{C}=\text{CH}_2$	+2.5
n-propyl ethylene (α - amylene).....	$\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2$	-6
Isopropyl ethylene (α -iso- amylene).....	$(\text{CH}_3)_2\text{CH}\cdot\text{CH}=\text{CH}_2$	+39
Sym. methyl ethyl ethylene (β -amylene).....	$\text{CH}_3\text{CH}_2\text{CH}=\text{CH}\cdot\text{CH}_3$	+21
Unsym. methyl ethyl ethylene (γ -amylene).....	$\text{CH}_3-\text{CH}_2-\text{C}(\text{CH}_3)=\text{CH}_2$	+36
Trimethyl ethylene (β -iso- amylene).....	$(\text{CH}_3)_2\text{C}=\text{CH}\cdot\text{CH}_3$	+31
Tetramethyl ethylene.....	$(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$	+36
		+73

The boiling points given in the table indicate that the four carbon atom members are gaseous at ordinary temperatures and that the five carbon atom members may readily exist in minor proportions in commercial gas mixtures, such as the cracked hydrocarbon gas mixtures with which the present invention is specially concerned.

The present process is particularly directed to the production of dimers and trimers from mono-olefins, particularly such olefins whose lower polymers boil at temperatures within the approximate range of commercial motor fuel, say, for example, from 100 to 400° F. It has been found that the dimers and some of the trimers of propylene, the butylenes and amylenes boil within this range and furthermore that these compounds have unusually high anti-knock characteristics. The following table shows the approximate boiling points of the dimers of propylene, butylenes, amylenes and hexylenes which will occur in appreciable quantities in the gases from oil cracking processes.

Boiling points of olefin dimers

Hexylene.....	155° F.
Octylene.....	255° F.
Decylene.....	323° F.
Dodecylene.....	417° F.

Of the lower boiling and normally gaseous olefins, ethylene is the most resistant to polymerization by catalysts of the present character, but in the presence of its higher homologues it is possible that a certain amount of mixed polymers are formed.

Polymers of higher molecular weight than the di- and tri-molecular compounds are generally of too high boiling point to be used in commercial gasolines and the end products of too extensive polymerization are resinous pitchy solids which are entirely unsuitable.

The essential ingredient of the solid catalysts which are employed in polymerizing olefins according to the present process is phosphoric acid, which in a majority of cases constitutes 80% or more of the catalyst mixture. Of the various acids of phosphorus, the orthophosphoric acid (H_3PO_4) is generally preferred on account of its polymerizing ability, its cheapness and the readiness with which it may be procured although the invention is not restricted to its use but may employ any of the other acids of phosphorus insofar as they are adaptable. It is not intended to infer, however, that the different acids of phosphorus which will be employed will produce identical polymerizing effects upon any given olefin or mixture of olefins, as each acid will exert its own characteristic action.

In using the preferred orthophosphoric acid, different concentrations may be employed from approximately 85 to 100% or acid containing some free phosphorus pentoxide may also be used. Within these concentration ranges, the acids will be thick liquids of varying viscosity and readily incorporated with the absorbent materials.

The main feature of the present invention resides in the employment of ordinarily liquid phosphoric acids as polymerizing catalysts in substantially solid form, this being accomplished by the alternative use of a number of different absorbent carrying materials which vary somewhat in their absorptive capacity and also in their chemical and physical properties and their influence upon the catalytic effect of the mixtures. The materials which may be employed are divisible roughly into two classes. The first class comprises materials of a predominately siliceous character and includes diatomaceous earth, kieselguhr and artificially prepared porous silica. In the case of naturally occurring diatoms it is believed that they sometimes contain minor amounts of highly active aluminum oxide which in some instances seems to contribute to the total catalytic effect of the solid catalyst. This active material is not present in the artificially prepared forms of silica.

The second class of materials which may be employed either alone or in conjunction with the first class (and with certain other optional ingredients to be later described) comprises generally certain members of the class of aluminum silicates and includes such naturally occurring substances as the various fuller's earths and clays such as bentonite, montmorillonite, et cetera. The class also includes certain artificially prepared aluminum silicates of which a purified aluminum silicate made by treating certain selected clays with hydrochloric or other mineral acid and washing out the reaction products is representative. The naturally occurring substances in this general class are characterized by a high adsorptive capacity which is particularly in evidence in making up the present type of phosphoric acid catalyst, and they may also contain traces of active ingredients which assist in producing the desired polymerizing effects. Again each substance which may be used alternatively will exert its own specific influence which will not necessarily be identical with that of the other members of the class.

In some cases the structure of the solid phos-

phoric acid catalyst may be improved by the primary incorporation of organic materials which yield a carbonaceous residue on heating. Substances which may be used in this manner include such materials as cellulose, starches, sugars, glue, gelatin, flour, molasses, agar-agar, et cetera. They evidently function as binders to some extent to prevent the breakdown of the catalyst structure when subjected to elevated temperatures and the action of hydrocarbon vapors or liquids in service.

Catalysts of the character comprised within the scope of the present invention are producible by a series of relatively simple steps comprising generally: mixing liquid phosphoric acid and the adsorbent materials in the selected proportions, heating at temperatures of approximately 180 to 220° C. and grinding and sizing the resultant product to produce particles of the desired size. The catalyst may be used in particle sizes of from approximately 4 to 20 mesh or may be made up into small briquettes. When carbonaceous materials are used somewhat higher temperatures may be employed to decompose them. The optimum temperature of heating when employing these materials varies considerably. Good results have been obtained at 300° C. and in some instances it would appear that too high temperatures above this point have a deleterious effect. The exact maximum temperature employed in the calcining step will be to some extent a matter of trial.

Catalysts of the present character are hygroscopic to a variable extent and are best ground, sized and preserved for use out of contact with moist air.

Owing to the possibility of varying the ingredients which go to form the catalyst masses, a number of alternatives exists each of which will have its own peculiar catalyzing and polymerizing character which will not be exactly equivalent to masses of different composition.

The polymerizing of gaseous olefins with catalysts of the present character may be brought about under numerous combinations of temperature and pressure, though the best results for any given pure olefin or mixture of olefins such as those encountered in the gases from oil cracking plants, will usually correspond to a particular set of conditions. It is a feature of the present type of catalyst that treatments may be conducted at temperatures as high as 250° C. and superatmospheric pressures up to several hundred pounds per square inch without danger of over-polymerization resulting in the formation of heavy tar-like polymers instead of liquids of gasoline boiling range.

In using the catalysts only simple equipment is necessary such as a tube or tower in which the catalyst is placed as a filling material. The gases may be pumped up to some given pressure and preheated to a suitable temperature prior to passage through the catalyst mass or the catalyst chamber may be heated externally if desired. A few test runs will usually determine the best conditions of operation. For example, if the temperatures and pressures employed are such that the products exist in vapor phase, the flow of the gases through the catalyst may be upward through filled towers while if liquids are condensed, the best results may be obtained when down flows are used so that liquid does not accumulate on the surface of the catalyst.

Solid phosphoric acid catalysts are character-

ized by their ability to polymerize olefins to produce relatively low boiling hydrocarbon polymers rather than heavy tars or pitches and by their long life due to the absence of such highly carbonaceous reaction products and also due to lack of oxidizing tendency in the phosphoric acid which constitutes the major portion thereof. In contrast to this it is notable that when employing sulfuric acid as a polymerizing agent, caution is necessary to prevent oxidation and undesirable side reactions such as ester formation and that, when employing metal halides such as aluminum chloride or zinc chloride, the tendency toward the formation of heavy polymers is very pronounced, so that it is not possible to produce more than minor amounts of desired low boiling hydrocarbons without the concurrent production of large quantities of heavy materials. Furthermore, such catalysts are readily regenerated after they have been contaminated by surface carbon deposits after long periods of service by merely burning off the deposits with air or other oxidizing gas at moderate temperatures. A still further advantage resides in the fact that they are substantially of a non-corrosive character as compared with the decided corrosive action of liquid phosphoric acid and other liquid polymerizing agents. The peculiar structural strength of catalyst masses of the present type has already been noted but may be mentioned again in connection with the general advantages which they possess, this being of special commercial value.

The following example of results obtained in polymerizing olefinic gases when using catalysts of the type comprised within the scope of the invention is characteristic though a number of others are available.

A catalyst was made by simply mixing 82 parts by weight of 89% commercial phosphoric acid and 18 parts by weight of kieselguhr. The semi-solid mass was heated to approximately 250° C. for a short time after which it was ground and sized to produce particles of from 4 to 10 mesh.

This catalyst was used in a vertical treating tube maintained at a temperature of 350° F. and a gas mixture from the stabilizer of an oil cracking plant (which contained 23% olefins including propylene and higher) was passed downwardly through the catalyst under a pressure of 100 pounds per square inch.

This operation produced 4.5 gallons of gasoline boiling range liquids for each 1000 cubic feet of gas mixture treated. The properties of the untreated product are shown in the following table, the figures being the average for a run of several days' duration.

Properties of gasoline hydrocarbons

Gravity, °A.P.I.	68.5
Initial boiling point	110° F
50% over at	240° F
90% over at	430° F
End boiling point	450° F
Distillation loss	3.5%
Color, Saybolt	26
Mg. of gum by copper dish	40
Octane number—research method	112

A light caustic treatment and a distillation to produce 410 end point product gave a gasoline satisfactory in all respects and stable under stor-

age with the addition of 0.01% of a commercial inhibitor consisting of a selected fraction of hard-wood tar.

The character of the invention and the marked commercial value thereof can be seen from a consideration of the preceding specification and the single instance of results given but neither is to be considered as imposing corresponding limitations upon the generally broad scope of the invention.

I claim as my invention:

1. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid and a solid adsorbent.

2. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid and a siliceous material.

3. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid and kieselguhr.

4. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid, siliceous material and an organic material which yields a carbonaceous residue on heating.

5. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid and an adsorbent earth.

6. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a phosphoric acid and a siliceous material containing aluminum oxide.

7. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined and briquetted mixture of a phosphoric acid and a solid adsorbent.

8. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined and briquetted mixture of a phosphoric acid and a siliceous material.

9. A process for the conversion of normally gaseous olefins into liquid hydrocarbons which comprises subjecting olefinic gas at polymerizing temperature to the action of a solid catalyst comprising a calcined mixture of a major proportion of a phosphoric acid and a minor proportion of a siliceous material.

VLADIMIR IPATIEFF.